

Rapid and Large-Scale Fabrication of Full Color Woodpile Photonic Crystals via Interference from a Conformal Multilevel Phase Mask

Sang-Hyeon Nam, Junyong Park,* and Seokwoo Jeon*

The practical use of photonic crystals with structural colors requires technology capable of rapidly producing large-area, three-dimensional (3D) periodic nanostructures. Until now, the fabrication of 3D photonic crystals has relied mainly on additive manufacturing and colloidal self-assembly. These technologies have provided a useful academic platform based on precisely controlled 3D periodicity but have not evolved into mass production technology. Here, optical lithography for the rapid fabrication of large-area 3D photonic crystals with structural colors is introduced. The key strategy is to incorporate two orthogonal line gratings (periodicity: 300 nm) made of an elastomer to create a conformal multilevel phase mask. When the mask is irradiated with a 355 nm laser, the five beam interference is established in the proximity region. The interlayer thickness between the two orthogonal line gratings controls the phase difference, which is closely related to the symmetry of the resulting 3D interference pattern. The interlayer thickness is designed to produce a woodpile structure with a planar periodicity of 300 nm and a vertical periodicity of 716 nm. The pattern area of the woodpile photonic crystal is expanded to 1 in². Red, green, and blue colors are experimentally realized by controlling the vertical shrinkage of the photoresist.

of a complete bandgap between the second and third bands even at a low refractive index contrast.^[11] In addition, the woodpile structure can be geometrically diversified through optical design.^[11] Based on these optical and structural strengths, the woodpile structure has been utilized for various optoelectronic applications to control light.^[12–14] However, the fabrication of such a useful woodpile structure with sub-micron periodicity for generating structural color is very challenging. Roughly, woodpile structures with submicron periodicity can be fabricated in two ways: 1) repeated rotation and stacking of binary nanostructures formed by unconventional planar nanopatterning^[15,16] and 2) serial lithography of 3D nanostructures using a highly focused laser source and the two-photon absorption effect.^[17,18] These approaches can generate very accurate woodpile structures at the nanoscale but are not suitable for rapid and large-scale production. Because of this difficulty in

nanofabrication, the size of experimental platforms with woodpile symmetry reported thus far is only approximately a few hundred micrometers. Additionally, the experimental angle-resolved reflection characteristics of woodpile photonic crystals in the visible wavelength region have not yet been intensively studied.

In this regard, optical 3D lithography employing an interference phenomenon has the potential to rapidly fabricate a woodpile structure with a visible color owing to its high-resolution patterning capability and diverse exposure geometries. In particular, proximity field nanopatterning (PnP) allows easy control of the 3D symmetry through the design of a conformal phase mask without intensive use of an optical setup.^[19–24] Generally, body-centered-tetragonal (BCT) is created by a single exposure through a conformal phase mask with a square or hexagonal grating.^[19,22] A dual exposure process using a binary phase mask is required to produce a diamond-like woodpile structure.^[25] In detail, after the first exposure of a photoresist film to light through a binary phase mask, the mask is rotated 90° to perform a second exposure. At this time, only a few hundred nanometers thick elastomeric spacer is required to optimize the spacing between the odd and even layers in the resulting woodpile structure. However, precisely rotating and aligning the binary phase mask with the spacer during the dual exposure

1. Introduction

3D photonic crystals with complete photonic bandgaps in the visible wavelength region are of interest to many researchers as next-generation optical materials that can realize low power passive displays,^[1–3] anti-counterfeiting holograms,^[4,5] solar cells,^[6,7] and exterior materials.^[8,9] Various structural unit cell symmetries have been theoretically proposed to realize such 3D photonic crystals with complete bandgaps.^[10] Among them, the diamond-like woodpile structure facilitates the implementation

S.-H. Nam, Prof. S. Jeon
Department of Materials Science and Engineering
KAIST Institute for the Nanocentury (KINC)
KAIST
Daejeon 34141, Republic of Korea
E-mail: jeon39@kaist.ac.kr

Prof. J. Park
School of Materials Science and Engineering
Kumoh National Institute of Technology
Gumi, Gyeongbuk 39177, Republic of Korea
E-mail: jpark@kumoh.ac.kr

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.201904971>.

DOI: 10.1002/adfm.201904971

process is very difficult. A more efficient way to create a woodpile structure using interference is to develop a multilevel phase mask that incorporates two orthogonal binary phase masks and a spacer into a single component.^[26,27] It is also challenging to align the two binary patterns orthogonally in a multilevel phase mask, but once it is made properly, mass production is available. This approach enables a single exposure process. In particular, a multilevel phase mask with a periodicity of 300 nm or less is required to produce a woodpile photonic crystal capable of reflecting color. In this patterning regime near the diffraction limit, an elastomer-based multilevel phase mask is highly desired to ensure conformal contact with the photoresist because the efficiency of the interference from the phase mask is extremely low.^[23] However, most of the multilevel phase masks reported thus far are made of rigid polymers, which does not guarantee the production of high-definition woodpile structures with photonic crystal properties.^[27–29] A conformal multilevel phase mask that can create well-defined woodpile structures with visible reflection colors over a large area has not yet been reported.

In this work, we first report inch-sized woodpile photonic crystals, which are designed to reflect various colors, produced by high-resolution PnP using a conformal multilevel phase mask with a periodicity of 300 nm. The conformal multilevel phase mask is simply prepared by plasma bonding two orthogonal binary phase masks made of poly(dimethylsiloxane) (PDMS). The thickness of the overcoated layer (interlayer) on the binary phase mask at the bottom of the multilevel phase mask is a key factor determining the phase difference and diffraction efficiency, which is related to the symmetry of the 3D interference pattern resulting from the phase mask. The interlayer thickness is optimized to $\approx 2.1 \mu\text{m}$, which is designed by optical simulation to generate the target woodpile symmetry.

The patterning area of the woodpile structure is 1 in^2 and maximum reflection is about 40 % in optical wavelength region. Its structural colors show a variety of ranging from blue to red depending on the vertical shrinkage of the photoresist, as determined by experimental parameters. Based on these results, inch-sized and pixelated woodpile photonic crystals are successfully realized through dose-controlled exposure or stepped postbaking with a gradient temperature.

2. Result and Discussion

Figure 1a illustrates the fabrication process of the conformal multilevel phase mask made of PDMS that allows conformal contact with the photoresist and enables the capture of evanescent waves for high-resolution patterning. The use of hard PDMS (h-PDMS) with a higher Young's modulus ($\approx 9 \text{ MPa}$) compared to soft PDMS (s-PDMS), represented by Sylgard 184 (Dow Chemical Co.), is generally required for successful replication of the submicron pattern from the Si master.^[30] The composition ratio between the monomer and cross linker of h-PDMS is slightly modified from the typical protocol^[31] to replicate the line and space pattern with a line width of 150 nm, a relief height of 150 nm, and a periodicity of 300 nm (Figure S1, Supporting Information). The first step in preparing the conformal multilevel phase mask is to prefabricate an ordinary bilayer phase mask with the target line and space pattern. Since bulk h-PDMS is rather brittle, a thin layer (approximately a few micrometers) of h-PDMS is first spin-coated on the Si master, and a thick s-PDMS layer is used as a back support. This bilayer elastomeric structure is commonly used for high-resolution conformal phase masks.^[19,20,31] In the PnP process, the laser is incident on the surface of the multilevel phase mask. The

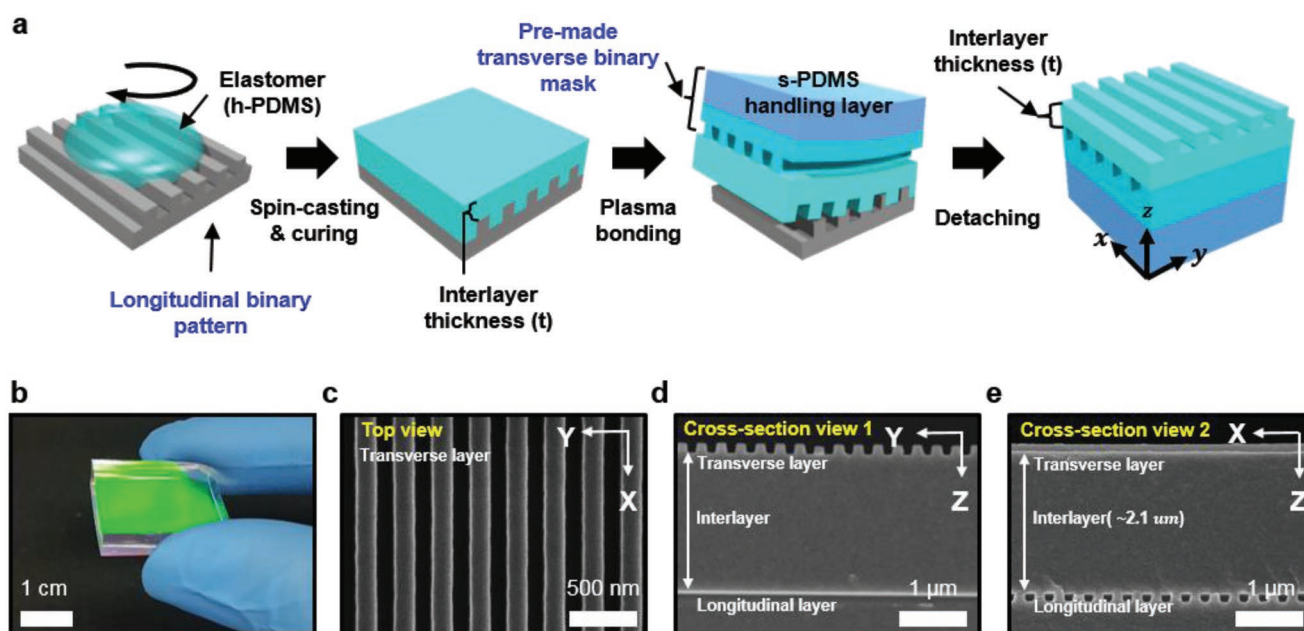


Figure 1. Preparation of a conformal multilevel phase mask. a) Schematic illustration of the fabrication procedures. b) Digital image of an inch-scale, conformal multilevel phase mask. c) Top-view SEM image of a transverse layer (XY plane) in a conformal multilevel phase mask. d) Cross-sectional SEM image of the YZ plane in a conformal multilevel phase mask. e) Cross-sectional SEM image of the XZ plane in a conformal multilevel phase mask.

second step is the formation of a thin h-PDMS layer on the Si master by spin-coating with controlled rotation speed and time. Precisely controlling the thickness of the overcoated h-PDMS layer on the Si master is important because this layer plays the role of an interlayer between the two orthogonal binary gratings, which is closely related to the phase difference and diffraction efficiency of the incident laser passing through the multilevel phase mask. The experimental interlayer thickness ranges from ≈ 1.8 to ≈ 4 μm by controlling the spin RPM (Figure S2, Supporting Information). The last step is the integration of the thin h-PDMS layer coated on the Si master and the premade bilayer phase mask. At this time, the bottom and top line and space patterns are aligned perpendicular to each other by matching linear edges of the pre-made binary phase mask and the spin-coated Si master with homemade jig. Permanent chemical bonding between them is achieved by oxygen termination via air plasma treatment, which is commonly used for microfluidic devices.^[32] For convenience, we set the line and space pattern with the periodic arrangement in the x-direction as the transverse layer and the line and space pattern with the periodic arrangement in the y-direction as the longitudinal layer. The two orthogonal layers are physically separated by the interlayer. Figure 1b shows a large-area (1 in.²) conformal multilevel phase mask successfully fabricated through the developed process. A top-view scanning electron microscopy (SEM) image shows a transverse layer consisting of a line and space pattern with a duty cycle of 50% (Figure 1c). The line and space pattern replicated from the Si master well maintains the

line width (≈ 150 nm) and spacing (≈ 150 nm) without significant defects. Two different cross-sectional SEM images of the conformal multilevel phase mask cut in 90° directions (corresponding to the xz and yz planes) prove that the transverse and longitudinal layers are orthogonally aligned to each other and separated by the interlayer (Figures 1d,e). Since all layers that make up the multilevel phase mask are made of PDMS, the interface of each layer appears to be seamless. To the best of our knowledge, this study is the first time that a monolithic and conformal multilevel phase mask with an ultrafine pitch of 150 nm has been experimentally realized. The developed inch-scale multilevel phase mask enables the rapid fabrication of a high-definition woodpile structure with visible reflection colors by a single exposure.

Figure 2a presents a schematic illustration of light propagation through the conformal multilevel phase mask during PnP. The incident light is circularly polarized, and the wavelength of the light is 355 nm. Figure 2b shows the number of diffractions expected to occur for the conformal multilevel phase masks with different grating periodicities in the x- and y-directions. In general, the five-beam interference condition is required to generate a woodpile structure.^[33–36] Considering the refractive index (≈ 1.66) of the photopolymer (SU-8, Microchem Co.), which is a well-known negative-tone thick resist for micro electro mechanical systems processing,^[37] four diffractions can be generated from the conformal multilevel phase mask with a grating periodicity of 300 nm, which results in the five beam interference condition. When light is transmitted through

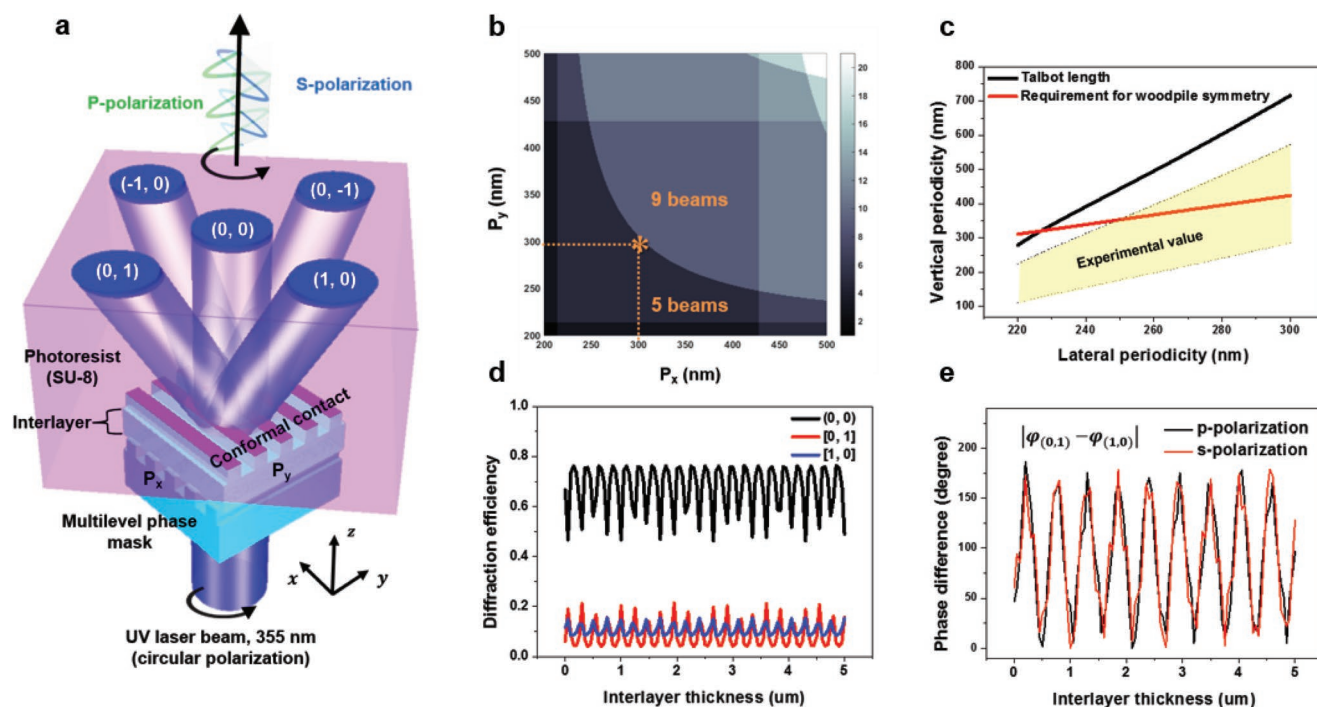


Figure 2. Optical aspects of a conformal multilevel phase mask. a) Schematic illustration of light propagation through a conformal multilevel phase mask. b) Calculated number of diffractions generated from conformal multilevel phase masks with different grating periodicities. c) Relation between the grating periodicity of a conformal multilevel phase mask and the resulting periodicity in the z-direction (black line: theoretical Talbot distance, red line: required periodicity for satisfying the woodpile symmetry with a unit cell of aspect ratio $1:\sqrt{2}$, yellow zone: experimental periodicity considering vertical shrinkage of the photopolymer during PnP). d) Diffraction efficiencies of first-order diffractions and transmitted beam according to the interlayer thickness. e) Phase differences between first-order diffractions according to the interlayer thickness.

the phase mask, a periodic light intensity distribution occurs along the z -direction as a result of Talbot interference.^[38,39] The periodicity in the z -direction is defined as the Talbot distance (Z_T)^[40,41]

$$Z_T = \frac{\lambda/n}{1 - \sqrt{1 - (\lambda/nP)^2}} \quad (1)$$

where P is the grating periodicity of the phase mask, n is the refractive index of the medium adjacent to the phase mask, and λ is the wavelength of the incident light. When the light is normally incident to the phase mask, the angle (θ) of the first-order diffractions is defined as

$$\theta = \sin^{-1}(\lambda/nP) \quad (2)$$

The unit cell of the woodpile structure must have a specific aspect ratio ($1:\sqrt{2}$), defined by the lateral to vertical lattice constants. Theoretically, when the angle of the first-order diffractions is 70.53° , the interference between the four first-order diffractions, assuming zeroth-order transmission is fully suppressed, and the transmitted beam can generate the woodpile symmetry with a unit cell of aspect ratio $1:\sqrt{2}$.^[33] From Equation (2), the grating periodicity of the multilevel phase mask satisfying this condition is approximately 226 nm. However, since the interference-based process can be regarded as a type of gray-scale lithography, the overall thickness of the pattern is generally reduced by up to $\approx 50\%$ depending on the degree of crosslinking.^[20] Therefore, to precisely control the unit cell of the resulting woodpile structure, the grating periodicity of the phase mask must be designed considering the experimental conditions (e.g., exposure dose and postbaking temperature and time) related to the vertical shrinkage of the photopolymer.^[33–36] Figure 2c presents the relation between the planar periodicity and vertical periodicity of the woodpile structure resulting from Talbot interference. The black line indicates the theoretical Talbot distance, and the red line indicates the periodicity required in the z -direction to satisfy the woodpile symmetry with the target unit cell of ratio $1:\sqrt{2}$. Theoretically, the target unit cell aspect ratio cannot be achieved because the Talbot distance is proportional to the square of the planar periodicity. However, considering the experimental factors, the vertical shrinkage of the photopolymer enables the realization of the woodpile structure with the target aspect ratio of unit cell. The yellow zone represents the range of experimental Talbot distances considering the vertical shrinkage of SU-8 reported in other studies.^[20,23,42] For example, assuming that the vertical shrinkage of the photopolymer is $\approx 59\%$, a vertical periodicity of ≈ 420 nm can be generated from the conformal multilevel phase mask with a grating periodicity of 300 nm. This result can be regarded as the angle of the first-order diffractions being reduced from 70.53° to 45.47° .

One of the important parameters in the geometrical design of the conformal multilevel phase mask is the interlayer thickness, which determines the diffraction efficiency of first-order diffractions and the phase difference between them. Generally, as the diffraction efficiency is increased by suppressing the directly transmitted beam (zeroth-order diffraction),

the pattern resolution becomes better due to the higher interference.^[22,23] Figure 2d shows the calculated diffraction efficiencies of two counterpropagating first-order diffractions ($[0\ 1]$, $[1\ 0]$) according to the interlayer thickness. In the case of a linearly polarized light source, the boundary conditions of the electromagnetic field directions in the multilevel phase mask with the two patterns are parallel to one binary pattern and vertical to the other. These most contrasting boundary conditions maximize the differences in the diffraction efficiencies for the two counterpropagating first-order diffractions. The diffraction efficiencies show the most even and least variation tendency as the interlayer thickness changes under circular polarization, which is attributed to the omnidirectional field distribution in the XY -plane and is expected to generate a uniform 3D structure.^[43] The polarization of the incident light for exposure is assumed to be circular polarization, which is insensitive to the direction (Figure 2d and Figures S3, Supporting Information). In case of linear polarizations, intensity distributions are biased in one axis (X or Y), which is expected to generate unequal 3D structures after PnP process (Figure S4, Supporting Information). The diffraction efficiencies are periodic with a periodicity of ≈ 291 nm as the interlayer thickness varies. The periodic patterns arise from the linear increase in the phase differences between the zeroth-order and first-order ($[1,0]$) diffractions in the interlayer region. Although no absorption is assumed in the PDMS region, the use of as thin an interlayer as possible is advantageous due to the slight absorption in the ultraviolet region in practice. In addition to the diffraction efficiencies, the interlayer thickness also affects the phase difference between the counterpropagating first-order diffractions, which finally determines the symmetry of the resultant Talbot interference. Figure 2e presents the phase difference between the diffractions as the interlayer thickness increases, with a periodicity of ≈ 582 nm. Due to the use of a circularly polarized light source, the phase comparison of the first-order diffractions is conducted by decomposing the polarization into p - and s -polarizations. Both polarizations show periodic phase variations as the interlayer thickness increases. Due to light propagation path differences between the zeroth-order and first-order ($[1, 0]$) beams after diffraction at the longitudinal layer, the phase difference linearly accumulates as the interlayer thickness increases (≈ 22 rad μm^{-1}). Second diffraction occurs at the transverse layer, and new orthogonal first-order beams ($[0, 1]$) interfere with the phase-modulated zeroth-order and first-order ($[1, 0]$) diffractions in the photoresist. The phase difference variation induces a shift of the relative distance between the interference images from the first- and second-order diffractions, which determines the symmetry of the 3D Talbot interference in the photoresist.^[27]

Figure 3 reveals the effect of the interlayer thickness or phase difference on the woodpile symmetry predicted by FDTD simulations (Lumerical Solutions Ltd.). Figure 3a displays the calculated light intensity distribution in the photopolymer SU-8 as a result of Talbot interference from the conformal multilevel phase mask with a periodicity of 300 nm. The phase difference between the counterpropagating first-order diffractions, which can be controlled by the interlayer thickness, is varied from 0° to 180° at an interval of 45° . The high intensity region in the photoresist will maintain the structure after

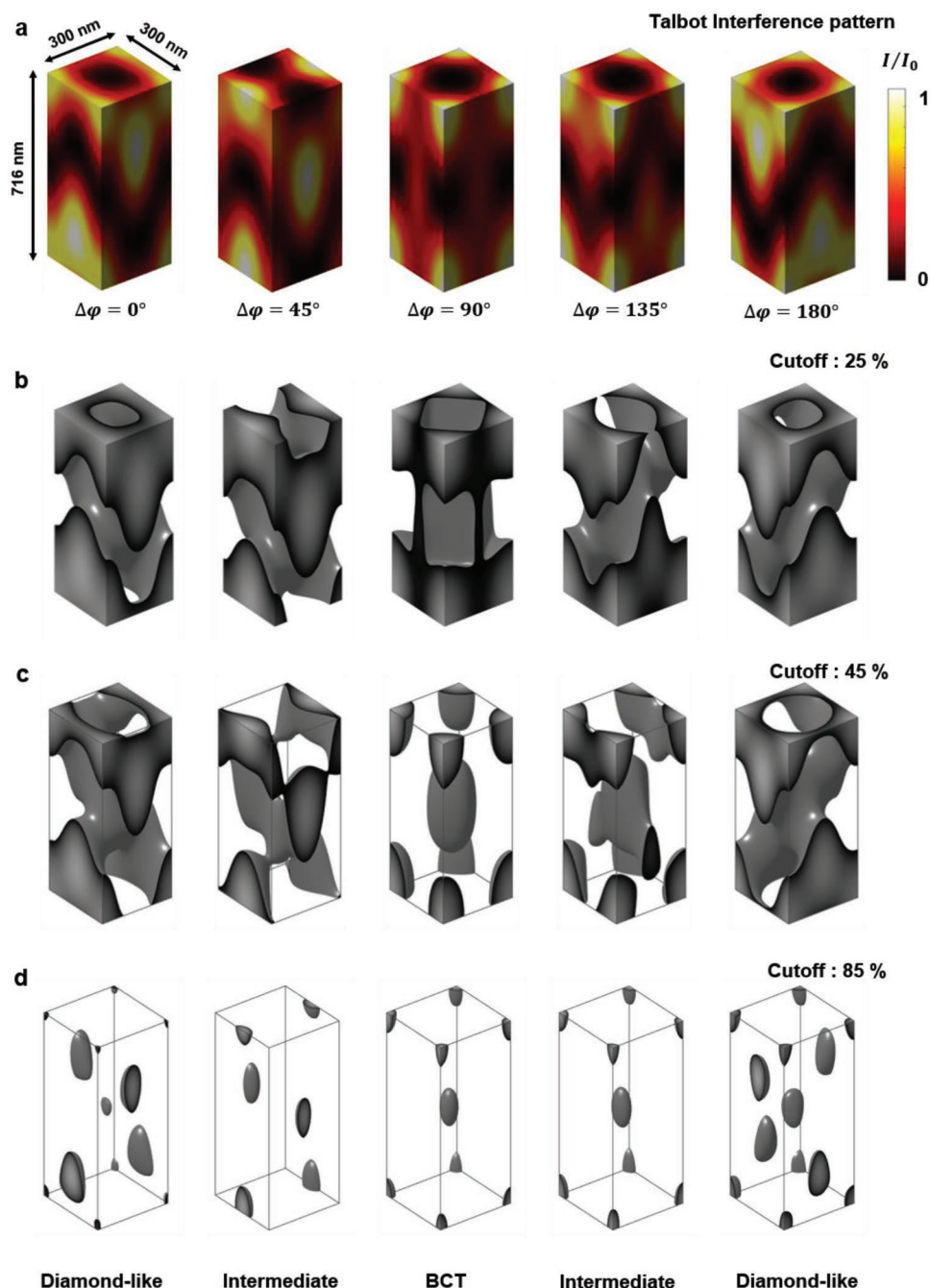


Figure 3. Finite-difference time-domain (FDTD) analysis of Talbot interference. a) Calculated light intensity distribution in a photopolymer (SU-8) according to the phase differences between first-order diffractions. b–d) Expected symmetry and fill factor for different cutoff filtering conditions (25, 45, and 85% of the maximum intensity).

the development process. Cutoff filtering of the intensity in the simulation results is conducted to visualize the expected unit cell structure (Figure 3b–d). The cutoff level, which is related to the experimental parameters (i.e., exposure dose and post-baking) in PnP, is adjusted from 25% to 85%. When the phase difference between two counterpropagating first-order diffractions is 90°, the BCT structure is generated. As the cutoff level increases, the fill factor of the unit cell gradually decreases, and the structure finally becomes lattice points when the cutoff

level reaches 85%. When the phase difference is 0° or 90° (corresponding to the thinnest interlayer thickness of ≈436 or 146 nm, respectively), the diamond-like woodpile symmetry is generated. The even layers in the structure are exactly located in the middle of the odd layer periodicity. At the cutoff level of 85%, diamond-like lattice points are clearly observed. When the phase difference is 45° or 135°, an intermediate structure between the BCT structure and the woodpile structure appears. Considering the uniformity of the thickness of the elastomeric

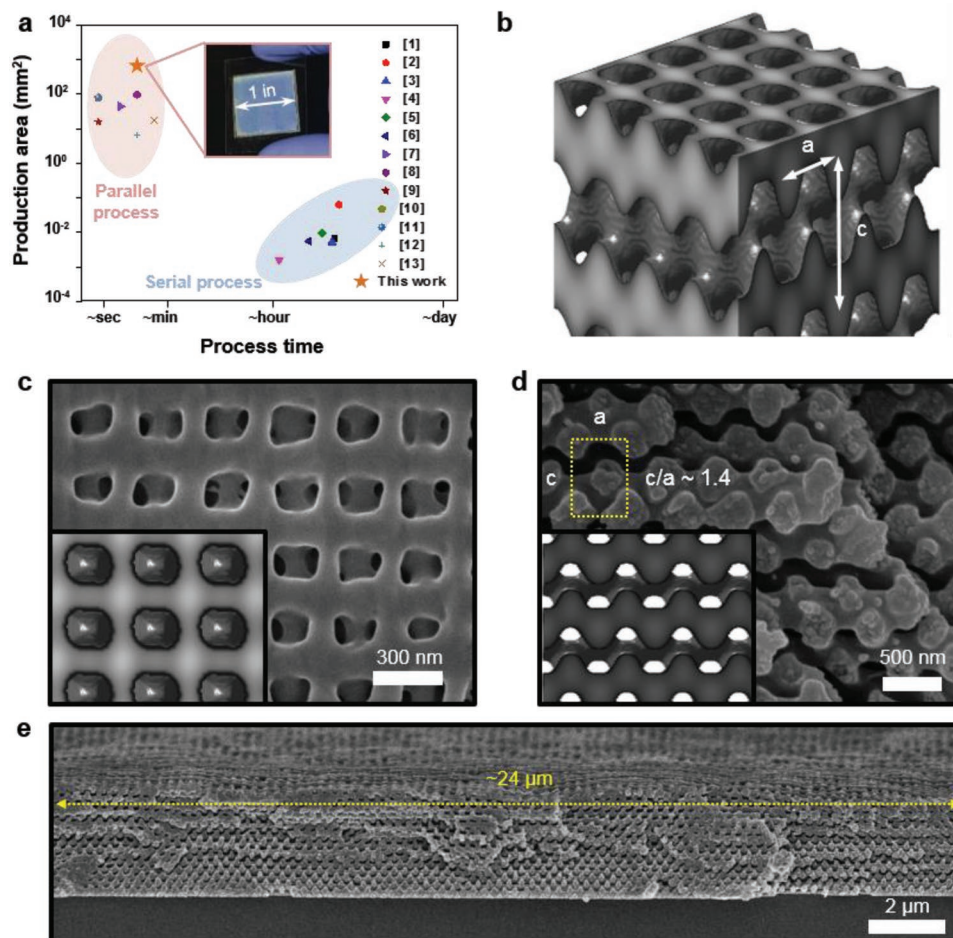


Figure 4. Rapid and large-scale fabrication of woodpile photonic crystal by PnP with a conformal multilevel phase mask. a) Comparison of throughput of fabrication techniques to manufacture a woodpile photonic crystal with submicron lateral and vertical periodicities (inset: digital image of an inch-scale woodpile photonic crystal formed by PnP using a conformal multilevel phase mask). b) Simulation of expected woodpile structure as a result of interference from a conformal multilevel phase mask with periodicity of 300 nm. c,d) SEM images of top and cross-sectional views of the fabricated woodpile photonic crystal. The lattice constants of a and c are ≈ 300 and ≈ 420 nm, respectively (inset: simulation results). e) SEM image of tilted-view of the fabricated woodpile photonic crystal.

thin film and the ease of handling, a $2.1 \mu\text{m}$ interlayer thickness, which can generate the woodpile symmetry, is selected for the experiment.

Figure 4 exhibits a large-area woodpile photonic crystal successfully fabricated via PnP with the conformal multilevel phase mask having an optimal interlayer thickness ($\approx 2.1 \mu\text{m}$). Basically, PnP can be regarded as a high throughput process because it can quickly create large-area woodpile structures in a single exposure. Compared to other techniques for manufacturing woodpile photonic crystals with submicron periodicity, PnP obviously has advantages in process time and production area (Table S1 in the Supporting Information and Figure 4a). A blueish color of the 1 in^2 optical film patterned by PnP proves that the resulting woodpile structure has a submicron periodicity that can reflect short wavelength visible light. (inset of Figure 4a). Figure 4b shows the theoretically expected woodpile structure and geometrical parameters generated by the used mask. The lateral periodicity of the fabricated woodpile structure is 300 nm, which is defined by the phase mask periodicity. When the vertical shrinkage of the photoresist of $\approx 59\%$ is compensated in the

FDTD simulation, the vertical periodicity of the fabricated woodpile structure is expected to be $\approx 420 \text{ nm}$.^[44] Figure 4c,d shows microscopic images of the woodpile structure fabricated via PnP. The insets show the simulation results, which well match the SEM images. The cross-sectional woodpile structure proves that the aspect ratio of the unit cell is experimentally reduced to ≈ 1.4 , similar to the target value for generating the woodpile symmetry, by optimizing the exposure dose ($\approx 18 \text{ mJ cm}^{-2}$) and postbaking conditions. This result implies that the aspect ratio of the unit cell can be further precisely controlled by adjusting the processing parameters such as the exposure dose and postbaking temperature and time. The large-scale woodpile structure without significant defects can be confirmed by Figure 4e. Inset digital image shows large-area woodpile photonic crystal successfully fabricated via PnP with the conformal multilevel phase mask having an optimal interlayer thickness ($\approx 2.1 \mu\text{m}$). The 1 in^2 optical film with the woodpile structure shows a blueish reflection color due to the submicron structural periodicity.

Figure 5 shows the optical characteristics of the woodpile photonic crystals fabricated with controlled process

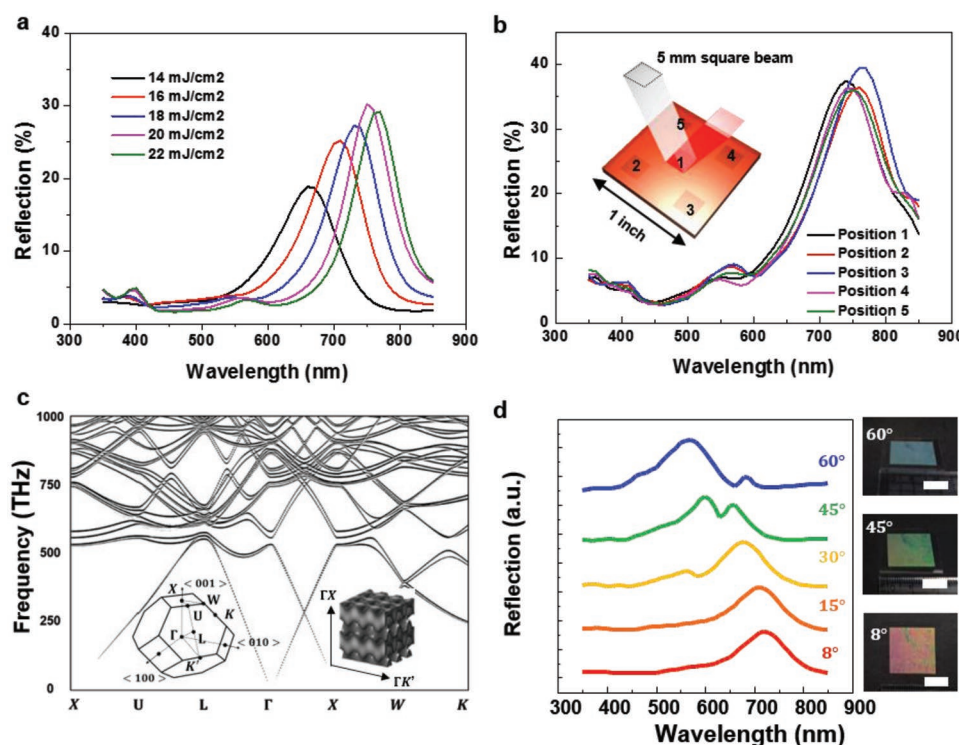


Figure 5. Optical properties of an inch-scale woodpile photonic crystal. a) Specular reflection spectra of woodpile photonic crystals fabricated with different exposure doses. b) Areal uniformity of specular reflection from the woodpile photonic crystal fabricated with an exposure dose of $\approx 22 \text{ mJ cm}^{-2}$ (inset: schematic of specular reflection measurement). c) Calculated photonic band structure of the woodpile photonic crystal. d) Angle-resolved specular reflection spectra of the woodpile photonic crystal, and digital images of reflection colors at different viewing angles (scale bar: 1 cm).

parameters. Unlike many previous studies that measured the reflection characteristics of photonic crystals in a microscopic region, we can evaluate the bulk reflectance properties using commercial equipment because the production area of the woodpile photonic crystals in this study is sufficiently large. Figure 5a displays the normal reflection spectra from the woodpile photonic crystals with different exposure doses ranging from 14 to 22 mJ cm^{-2} . The postbaking for all samples is identically conducted at 55°C for 15 min. When the exposure dose is 14 mJ cm^{-2} , the main reflection peak occurs at 660 nm, and the reflectance is 19%. As the exposure dose increases, the main reflection peak redshifts, and the reflectance increases. In general, a higher energy dose causes a higher crosslinking density of the photopolymer, resulting in less shrinkage after development.^[34–36] Thus, the Bragg reflection occurs at longer wavelengths. The increase in the reflectance is related to the structural fill factor.^[18] When the exposure dose is 22 mJ cm^{-2} , the main reflection peak occurs at 740 nm, and the reflectance reaches 30%. The reflectance data for more experimental conditions can be found in Figure S5 (Supporting Information). Figure 5b presents the areal uniformity of the fabricated woodpile photonic crystal film. The reflection spectra are measured at five different positions in a 1 in^2 film. The reflection properties (i.e., peak location and intensity) for each point are very similar. To improve reflection, it is crucial to reduce local defects caused by dust and structural irregularities, which come from shrinkage and swelling of the SU-8 photoresist during lithography process.

The calculated band structure shows that a complete bandgap does not naturally occur in the woodpile structure due to the low refractive index (≈ 1.66) of the SU-8 photoresist (Figure 5c). If the constituent material is changed to TiO_2 , whose refractive index is ≈ 2.4 , through the established material conversion process,^[23,45–49] then a complete bandgap can be realized in the woodpile structure (Figure S6, Supporting Information). Figure 5d shows the angle-resolved reflection spectra of the inch-scale woodpile photonic crystal made of SU-8. When the light is incident on the sample at a larger angle, the main reflection peak is blueshifted. This blueshift is caused by the intrinsic angular dependence of the Bragg reflection. Above a critical angle (30°), peak separation is observed. The emergence of doublet peaks can be interpreted as a transition of the Bragg plane.^[50,51] Generally, before reaching the critical angle, only the (001) plane acts as a Bragg reflection site. However, above the critical angle, another plane becomes a resonant Bragg reflection plane, resulting in the emergence of a new peak in the spectra. If the incident angle is further increased, then the intensity of the emerging reflection peak from the resonant plane overwhelms the peak corresponding to the (001) plane. This angle-resolved reflection spectrum verifies the well-defined woodpile structure with multiple resonant planes.

Figure 6 demonstrates the patterning capabilities of PnP for realizing multicolor pixelation with woodpile photonic crystals. Basically, the reflection color can be controlled by the exposure dose. The pixelation of an inch-scale woodpile photonic crystal is achieved by dose control using an additional amplitude mask

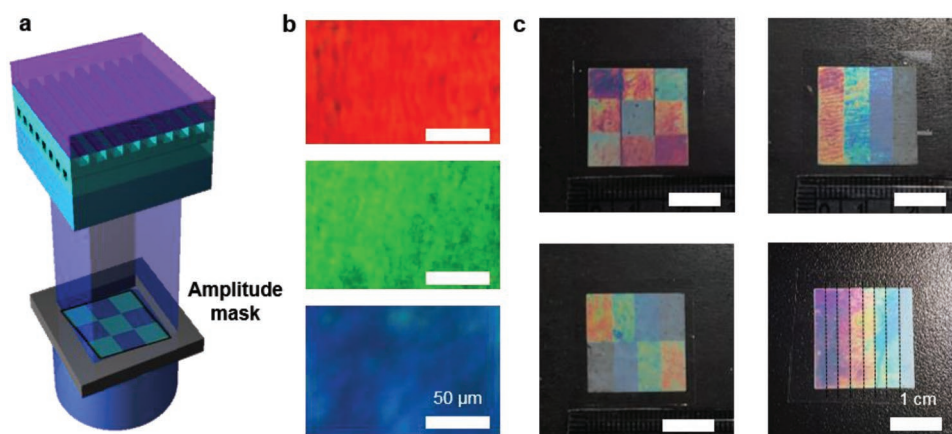


Figure 6. Pixelated inch-scale woodpile photonic crystal. a) Schematic illustration of the modified PnP process with a spatial filter for generating pixelated colors. b) Optical microscope images of three different zones (red, green, and blue) in a pixelated woodpile photonic crystal. c) Various pixelated multicolor patterns obtained using amplitude masks with different geometries.

(Figure 6a). First, the entire area is lightly exposed to patterning light through a conformal multilevel phase mask to create a blue reflection color. The selected area is then exposed with the aid of a patterned amplitude mask to accumulate the energy dose. Depending on the accumulated energy dose, shiny RGB colors can be reproducibly realized (Figure 6b). Various types of pixels can be produced by designing different patterns of the amplitude mask (Figure 6c). In addition, gradient coloration can also be achieved by a modified postbaking process with a gradient temperature, which is another way to control the crosslinking density of the photopolymer (Figure S7, Supporting Information). The setup for generating the gradient temperature involves positioning the substrate on a hot plate by tilting it like a slide. The degree of the temperature gradient is confirmed by an infrared camera (Figure S7b, Supporting Information). The higher postbaking temperature zone enables a higher crosslinking density and less vertical shrinkage of the photopolymer, resulting in a reflection color of a longer wavelength. The continuous gradient temperature produces a woodpile photonic crystal film with iridescent colors at the same angle (Figure S7c, Supporting Information).

3. Conclusion

In this work, a large-scale visible woodpile structure is fabricated by a single exposure process with a conformal multilevel phase mask. To generate a woodpile structure with submicron unit cell periodicity, a conformal multilevel phase mask with an ultrafine pitch of 300 nm is used for the fabrication. The effect of the thickness of the interlayer between the two orthogonal gratings on the phase difference and the diffraction efficiency is thoroughly evaluated by FDTD simulations. The interlayer thickness is optimized to $\approx 2.1 \mu\text{m}$ to generate the woodpile symmetry with a unit cell aspect ratio of ≈ 1.4 . The resulting inch-scale woodpile photonic crystals show bulk reflection ($\approx 30\%$) in the visible wavelength region, and the colors can be finely tuned by adjusting the process parameters. By integrating an amplitude mask into the PnP optical setup, pixelated multicolor patterns are successfully realized through exposure dose

control. The rapid and large-scale fabrication ability of the technique developed in this study will enable the practical application of 3D photonic crystals in advanced optoelectronic devices and as exterior materials. Further optimization for scale-up process with roll-to-roll or scanning methods could extend its application for aerospace components, building exterior materials, solar cells, apparel, and passive displays. Exploring the multifunctionality or tuning the photonic crystal properties through conformal coating of inorganic materials on woodpile structures will be a promising future research direction.^[46,52]

4. Experimental Section

Preparation of the Conformal Multilevel Phase Mask: PDMS was selected as the constituent material of the conformal multilevel phase mask. The patterned region was prepared with h-PDMS and a thick layer for handling of s-PDMS. The h-PDMS component weight ratio was set to replicate the line and space pattern with a 300 nm period: 2.93 g of vinyl PDMS prepolymer (VDT-731, Gelest Corp.), 0.06 g of a modulator (87927, Sigma-Aldrich), 0.03 g of a platinum catalyst (SIP6831.1, Gelest), and 1.47 g of hydrosilane prepolymer (HMS-301, Gelest). The mixing process was conducted by a protocol step using a planetary mixer (ARE-310, Thinky) at 2000 rpm. Then, h-PDMS was spin-coated onto the Si line and space master at 4000 rpm for 10–15 min, and the master was treated with a self-assembled monolayer (SIT8174.0, Gelest). Air plasma treatment (45 sccm, 40 mTorr, 60 W) was applied to the patterned premade linear PDMS mold and spin-coated area of the Si master for 1 min. After aligned contact of the premade mold with the spin-coated area, the sample was placed in an oven over 1 h. Then, the mask was detached from the Si master.

Optical Design of the Multilevel Phase Mask: The number of diffraction orders for different lateral periods of the multilevel phase mask and diffraction efficiencies was calculated by the finite-difference time-domain method (FDTD, Lumerical). Circularly polarized light was injected normally to a unit of multilevel phase mask structure with lateral periodic boundaries and perfectly matched-layer (PML) boundaries at the end of optical axis. Data of diffracted beams were retrieved by grating analysis tool in the software library including number of diffraction, s- and p-polarization phase, diffraction efficiencies, and propagation angles. 3D interference field data in the photoresist film were calculated with resolution of 5 nm or 10 nm cubic voxel. The resultant 3D Talbot images were processed to the 3D template structure using the level-set method.^[53] The modeled unit cell of woodpile structure was analyzed to access band structure by the FDTD method.

Fabrication of the Woodpile Structure by the PnP Process: The multilevel phase mask was placed on the surface of a 10 μm thick photoresist film (SU-8, Microchem) supported by a cured 2 μm SU-8 adhesion layer on cover glass. After conformal contact, a laser beam (355 nm, 300 mW, Nd:YAG, Advanced Optowave) was used to irradiate the photoresist film through the multilevel mask in collimated and expanded states via an optical setup. The exposure dose ranged from 14 to 24 mJ cm^{-2} . An additional curing process was performed through postexposure baking, adjusting the temperature (50–60 $^{\circ}\text{C}$) and time (5–20 min). Only the exposed region over the cutoff dose remained in the developer (SU-8 developer, Microchem), and finally, the sample was rinsed and dried via a supercritical drying process (R-401, ChemreSys).

Characterizations: The multilevel phase mask and 3D nanostructure of the woodpile photonic crystal were visualized by a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi) with an accelerating voltage of 5 kV. The samples were cut using a blade for the multilevel mask and a diamond cutter for the woodpile photonic crystal and then coated by osmium for SEM imaging (HPC-1SW, Vacuum Devices). Specular reflections of the sample were measured using a UV–vis/NIR spectrophotometer (Lambda 1050, Perkin Elmer) with incident angle variation from 8 $^{\circ}$ for normal incidence to 60 $^{\circ}$ using a silver mirror as a reference. The sampling area was set to 5 $\times$ 5 mm^2 .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This study was also supported by the National Research Foundation (NRF) of Korea funded by the Ministry of Science and ICT and Future Planning (MSIP) (2016R1E1A1A01943131) and the Multi-Ministry Collaborative R&D Program (Development of Techniques for Identification and Analysis of Gas Molecules to Protect Against Toxic Substances) through the National Research Foundation of Korea (NRF) funded by KNPA, MSIT, MOTIE, ME, and NFA (2017M3D9A1073501).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

full color, multilevel phase mask, photonic crystal, proximity field nanopatterning, woodpile structure

Received: June 21, 2019

Revised: August 4, 2019

Published online:

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